Executive Summary

ES.1 Introduction

The capability of chemical substances to undergo reactions, or transformations in their structure, is central to the chemical processing industry. Chemical reactions allow for a diversity of manufactured products. However, chemical reactivity can lead to significant hazards if not properly understood and controlled.

Reactivity\(^1\) is not necessarily an intrinsic property of a chemical substance. The hazards associated with reactivity are related to process-specific factors, such as operating temperatures, pressures, quantities handled, concentrations, the presence of other substances, and impurities with catalytic effects.

Safely conducting chemical reactions is a core competency of the chemical manufacturing industry. However, chemical reactions can rapidly release large quantities of heat, energy, and gaseous byproducts. Uncontrolled reactions have led to serious explosions, fires, and toxic emissions. The impacts may be severe in terms of death and injury to people, damage to physical property, and effects on the environment. In particular, incidents at Napp Technologies in 1995 and Morton International in 1998 raised concerns about reactive hazards to a national level. These and other incidents across the United States\(^2\) underscore the need to improve the management of reactive hazards.

\(^1\) See Appendix A, Glossary, for a definition of “reactivity” and numerous other technical terms.

\(^2\) For example: BPS, Inc., West Helena, Arkansas (1997), with three fatalities; Condea Vista, Baltimore, Maryland (1998), with five injured; Whitehall Leather Company, Whitehall, Michigan (1999), with one fatality; and Concept Sciences, Inc., Allentown, Pennsylvania (1999), with five fatalities and 14 injured.
A variety of legal requirements and regulations govern the hazards associated with highly hazardous chemicals (including reactive chemicals), among which are regulations of the Occupational Safety and Health Administration (OSHA) and the U.S. Environmental Protection Agency (EPA).

OSHA develops and enforces standards to protect employees from workplace hazards. In the aftermath of the reactive incident that caused the Bhopal tragedy,1 OSHA was concerned about the possibility of a catastrophe at chemical plants in the United States. Its own investigations in the mid-1980s indicated a need to look beyond existing standards.

Bhopal and a series of other major incidents underscored the need for increased attention to process safety management; OSHA began to develop a standard that would incorporate these principles. A proposed standard was published in 1990. Additionally, the Clean Air Act Amendments (CAAAA) of 1990 required OSHA to promulgate a standard to protect employees from the hazards associated with releases of highly hazardous chemicals, including reactive chemicals.

In 1992, OSHA promulgated its process safety management (PSM) standard (29 CFR 1910.119). The standard covers processes containing individually listed chemicals that present a range of hazards, including reactivity, as well as a class of flammable chemicals. Reactive chemicals were selected from an existing list of chemicals identified and rated by the National Fire Protection Association (NFPA) because of their instability rating of “3” or “4” (on a scale of 0 to 4).2,3

CAAAA also required EPA to develop regulations to prevent the accidental release of substances, including reactives, that could have serious effects on the public or the environment. In 1996, EPA

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1 On December 4, 1984, approximately 40 metric tons of methyl isocyanate was accidentally released in Bhopal, India. The incident resulted in an estimated 2,000 deaths within a short period (Lees, 1996; App. 5).

2 OSHA used the 1975 version of NFPA 49, Hazardous Chemicals Data

3 An NFPA instability rating of “4” means that materials in themselves are readily capable of detonation or explosive decomposition or explosive reaction at normal temperatures and pressures. A rating of “3” means that materials in themselves are capable of detonation or explosive decomposition or explosive reaction, but require a strong initiating source or must be heated under confinement before initiation.
promulgated its Accidental Release Prevention Requirements (40 CFR Part 68) in response to the congressional mandate. Although this standard established new measures with regard to public notification, emergency response, and accident reporting, its requirements for managing process safety are similar to those of the OSHA PSM Standard. For purposes of this regulation, EPA identified covered substances based on toxicity and flammability— but not chemical reactivity.

Professional and trade associations such as the American Institute of Chemical Engineers (AIChE), the American Chemistry Council (ACC), the Synthetic Organic Chemical Manufacturers Association (SOCMA), and the National Association of Chemical Distributors (NACD) provide voluntary chemical process safety guidance to their members.

In 1985, AIChE established the Center for Chemical Process Safety (CCPS) in response to the Bhopal tragedy. Manufacturers, government, and scientific research groups sponsor CCPS, which has published extensive industry guidance in the area of process safety technology and management. CCPS recently produced a safety alert on reactive hazards, and a more comprehensive product is under development.

ACC and SOCMA each have programs to promote good practices among member companies in the area of chemical process safety. Similarly, NACD promotes good distribution practices and dissemination of information to end-use customers on the proper handling of chemical products.

This report, *Hazard Investigation: Improving Reactive Hazard Management*, by the U.S. Chemical Safety and Hazard Investigation Board (CSB), examines chemical process safety in the United States— specifically, hazardous chemical reactivity. Its objectives are to:

- Determine the impacts of reactive chemical incidents.
- Examine how industry, OSHA, and EPA currently address reactive chemical hazards.
Determine the differences, if any, between small, medium, and large companies with regard to reactive chemical policies, practices, in-house reactivity research, testing, and process engineering.

Analyze the appropriateness of, and consider alternatives to, industry and OSHA use of the NFPA instability rating system for process safety management.

Develop recommendations for reducing the number and severity of reactive chemical incidents.

ES.2 Investigative Process

CSB completed the following tasks:

- Analyzed reactive incidents by collecting and reviewing available data.
- Surveyed current reactive hazard management practices in industry.
- Visited companies to observe reactive hazard management practices.
- Analyzed regulatory coverage of reactive hazards.
- Met with stakeholders to discuss the problem and approaches to improve the management of reactive hazards.
- Conducted a public hearing at which further stakeholder inputs were solicited on key findings and preliminary conclusions from the hazard investigation.

The data analysis included evaluating the number, impact, profile, and causes of reactive incidents. CSB examined more than 40 data sources (e.g., industry and governmental databases and guidance documents; safety/loss prevention texts and journals; and industry association, professional society,
insurance, and academic newsletters), focusing on incidents where the primary cause was related to chemical reactivity.

For the purposes of this investigation, an “incident” is defined as a sudden event involving an uncontrolled chemical reaction—with significant increases in temperature, pressure, and/or gas evolution—that has caused, or has the potential to cause, serious harm to people, property, or the environment.

Through a survey of select small, medium, and large companies, information was gathered about good practices for reactive hazard management within the chemical industry. CSB also visited chemical industry facilities that have implemented programs for managing reactive hazards.

**ES.3 Key Findings**

1. The limited data analyzed by CSB include 167 serious incidents in the United States involving uncontrolled chemical reactivity from January 1980 to June 2001. Forty-eight of these incidents resulted in a total of 108 fatalities. The data include an average of six injury-related incidents per year, resulting in an average of five fatalities annually.

2. Nearly 50 of the 167 incidents affected the public.\(^6\)

3. Over 50 percent of the 167 incidents involved chemicals not covered by existing OSHA or EPA process safety regulations.\(^7\)

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\(^6\) “Public impact” is defined as known injury, offsite evacuation, or shelter-in-place.

4. Approximately 60 percent of the 167 incidents involved chemicals that either are not rated by NFPA or have “no special hazard” (NFPA “0”). Only 10 percent of the 167 incidents involved chemicals with NFPA published ratings of “3” or “4.”

5. For the purpose of the OSHA PSM regulation, NFPA instability ratings have the following limitations with respect to identifying reactive hazards:

- They were originally designed for initial emergency response purposes, not for application to chemical process safety.
- They address inherent instability only, not reactivity with other chemical substances (with the exception of water) or chemical behavior under nonambient conditions.
- NFPA Standard 49—on which the OSHA PSM-listed highly reactive chemicals are based—covers only 325 chemical substances, a very small percentage of the chemicals used in industry.
- The OSHA PSM Standard lists 137 highly hazardous chemicals—only 38 of which are considered highly reactive based on NFPA instability ratings of “3” or “4.”
- The NFPA ratings were established by a system that relies, in part, on subjective criteria and judgment.

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8 An NFPA instability rating of “0” means that materials in themselves are normally stable, even under “fire” conditions.
10 The Chemical Abstracts Service maintains data on over 200,000 chemicals that are listed under national and international regulations.
6. As a result of the joint OSHA-EPA chemical accident investigation of the Napp Technologies incident in April 1995, a recommendation was made by EPA and OSHA to consider adding more reactive chemicals to their respective lists of chemicals covered by process safety regulations. To date, neither OSHA nor EPA process safety regulations have been modified to better cover reactive hazards.

7. Reactive hazards are diverse. The reactive incident data analyzed by CSB included:

- Over 40 different chemical classes (i.e., acids, bases, monomers, oxidizers, etc.), with no single dominating class.

- Several types of hazardous chemical reactivity, with 36 percent attributed to chemical incompatibility, 35 percent to runaway reactions, and 10 percent to impact-sensitive or thermally sensitive materials.

- A diverse range of chemical process equipment—including reaction vessels, storage tanks, separation equipment, and transfer equipment. Storage and process equipment (excluding chemical reaction vessels) account for over 65 percent of the equipment involved; chemical reaction vessels account for only 25 percent.

Reactive incidents can result in a variety of consequences, including fire and explosions (42 percent of incidents) as well as toxic gas emissions (37 percent).

8. No one comprehensive data source contains the data needed to adequately understand root causes and lessons learned from reactive incidents or other process safety incidents.

9. Incident data collected by OSHA and EPA provide no functional capability to track reactive incidents so as to analyze incident trends and develop preventive actions at a national level.
10. Causes and lessons learned are reported in only 20 percent of the 167 incidents. (Industry associations, government agencies, and academia typically do not collect this information.) However, more than 60 percent of the incidents for which some causal information was available involved inadequate practices for identifying hazards or conducting process hazard evaluations; nearly 50 percent involved inadequate procedures for storage, handling, or processing of chemicals.\textsuperscript{11}

11. Over 90 percent of the incidents analyzed by CSB involved reactive hazards that are documented in publicly available literature accessible to the chemical processing and handling industry.\textsuperscript{12}

12. Although several computerized tools\textsuperscript{13} and literature resources are available to identify reactive hazards, surveyed companies do not generally use them. In some cases, these tools provide an efficient means of identifying reactive hazards without the need for chemical testing.

13. Surveyed companies share chemical data of a general nature for most chemicals (e.g., material safety data sheets [MSDS]) and good handling practices for some. However, detailed reactive chemical test data, such as thermal stability data—which can be valuable in identifying reactive hazards—are not typically shared.

14. Approximately 70 percent of the 167 incidents occurred in the chemical manufacturing industry. Thirty percent involved a variety of other industrial sectors that store, handle, or use chemicals in bulk quantities.

\textsuperscript{11}The summation of causal factor statistics exceeds 100 percent because each major incident can, and often does, have more than one cause.
\textsuperscript{12} See Section 6.1 for a list of selected literature.
\textsuperscript{13}National Oceanic and Atmospheric Administration (NOAA) Chemical Reactivity Worksheet, American Society for Testing and Materials (ASTM) CHETAH, and Bretherick’s Database of Reactive Chemical Hazards.
15. Only limited guidance on the management of reactive hazards throughout the life cycle of a chemical manufacturing process is currently available to industry through professional societies, standards organizations, government agencies, or trade associations. There are significant gaps in the following:

- Unique aspects of reactive hazards that should be examined during process hazard analysis (PHA), such as the need for reactive chemical test data, and methods to identify and evaluate worst case scenarios involving uncontrolled reactivity.

- Integration of reactive hazard information into process safety information, operating procedures, training, and communication practices.

- Review of the impact on reactive hazards due to proposed changes in chemical processes.

- Concise guidance targeted at companies engaged primarily in the bulk storage, handling, and use of chemicals to prevent inadvertent mixing of incompatible substances.

16. Several voluntary industry initiatives, such as ACC’s Responsible Care and NACD’s Responsible Distribution Process (RDP), provide guidance on process safety management for chemical manufacturers and distributors. However, no voluntary industry initiatives list specific codes or requirements for reactive hazard management.

17. The EPA RMP regulation and the European Community’s Seveso II directive both exempt covered processes from some regulatory provisions, if the facility documents the absence of catastrophic damage from process accidents under reasonable worst case conditions. The State of New Jersey is also considering similar action in its proposed revisions of the Toxic Catastrophe Prevention Act (TCPA) regulations.

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14 A recently initiated CCPS project, Managing Reactive Chemical Hazards, may address this gap in industry guidance.
ES.4 Conclusions

1. Reactive incidents are a significant chemical safety problem.

2. The OSHA PSM Standard has significant gaps in coverage of reactive hazards because it is based on a limited list of individual chemicals with inherently reactive properties.

3. NFPA instability ratings are insufficient as the sole basis for determining coverage of reactive hazards in the OSHA PSM Standard.

4. The EPA Chemical Accident Prevention Requirements (40 CFR 68) have significant gaps in coverage of reactive hazards.

5. Using lists of chemicals is an inadequate approach for regulatory coverage of reactive hazards. Improving reactive hazard management requires that both regulators and industry address the hazards from combinations of chemicals and process-specific conditions rather than focus exclusively on the inherent properties of individual chemicals.

6. Reactive incidents are not unique to the chemical manufacturing industry. They also occur in many other industries where chemicals are stored, handled, or used.

7. Existing sources of incident data are not adequate to identify the number, severity, and causes of reactive incidents or to analyze incident frequency trends.

8. There is no publicly available database for sharing lessons learned from reactive incidents.

9. Neither the OSHA PSM Standard nor the EPA RMP regulation explicitly require specific hazards, such as reactive hazards, to be examined when performing a process hazard analysis. Given that reactive incidents are often caused by inadequate recognition and evaluation of reactive hazards, improving reactive hazard management involves defining and requiring
relevant factors (e.g., rate and quantity of heat and gas generated) to be examined within a process hazard analysis.

10. The OSHA PSM Standard and EPA RMP regulation do not explicitly require the use of multiple sources when compiling process safety information.

11. Publicly available resources\(^{15}\) are not always used by industry to assist in identifying reactive hazards.

12. There is no publicly available database to share reactive chemical test information.

13. Current good practice guidelines on how to effectively manage reactive hazards throughout the life cycle\(^{16}\) of a chemical manufacturing process are neither complete nor sufficiently explicit.

14. Given the impact and diversity of reactive hazards, optimum progress in the prevention of reactive incidents requires both enhanced regulatory and nonregulatory programs.

\(^{15}\) NOAA Chemical Reactivity Worksheet, ASTM CHETAH, and Bretherick’s Database of Reactive Chemical Hazards.

\(^{16}\)“Life cycle” refers to all phases of a chemical manufacturing process–from conceptualization, process research and development (R&D), engineering design, construction, commissioning, commercial operation, and major modification to decommissioning.
ES.5 Recommendations

Occupational Safety and Health Administration (OSHA)

1. Amend the Process Safety Management (PSM) Standard, 29 CFR 1910.119, to achieve more comprehensive control of reactive hazards that could have catastrophic consequences.

   - Broaden the application to cover reactive hazards resulting from process-specific conditions and combinations of chemicals. Additionally, broaden coverage of hazards from self-reactive chemicals. In expanding PSM coverage, use objective criteria.
   Consider criteria such as the North American Industry Classification System (NAICS), a reactive hazard classification system (e.g., based on heat of reaction or toxic gas evolution), incident history, or catastrophic potential.

   - In the compilation of process safety information, require that multiple sources of information be sufficiently consulted to understand and control potential reactive hazards. Useful sources include:

     - Literature surveys (e.g., Bretherick’s *Handbook of Reactive Chemical Hazards*, Sax’s *Dangerous Properties of Industrial Materials*).

     - Information developed from computerized tools (e.g., CHETAH, NOAA’s The Chemical Reactivity Worksheet).

     - Chemical reactivity test data produced by employers or obtained from other sources (e.g., differential scanning calorimetry, thermogravimetric analysis, accelerating rate calorimetry).

     - Relevant incident reports from the plant, the corporation, industry, and government.

     - Chemical Abstracts Service.
• Augment the process hazard analysis (PHA) element to explicitly require an evaluation of reactive hazards. In revising this element, evaluate the need to consider relevant factors, such as:

- Rate and quantity of heat or gas generated.
- Maximum operating temperature to avoid decomposition.
- Thermal stability of reactants, reaction mixtures, byproducts, waste streams, and products.
- Effect of variables such as charging rates, catalyst addition, and possible contaminants.
- Understanding the consequences of runaway reactions or toxic gas evolution.

2. Implement a program to define and record information on reactive incidents that OSHA investigates or requires to be investigated under OSHA regulations. Structure the collected information so that it can be used to measure progress in the prevention of reactive incidents that give rise to catastrophic releases.

**U.S. Environmental Protection Agency (EPA)**

1. Revise the Chemical Accident Prevention Programs, 40 CFR 68 (RMP), to explicitly cover catastrophic reactive hazards that have the potential to seriously impact the public, including those resulting from self-reactive chemicals and combinations of chemicals and process-specific conditions. Take into account the recommendations of this report to OSHA on reactive hazard coverage. Seek congressional authority if necessary to amend the regulation.

2. Modify the accident reporting requirements in RMP*INFO to define and record reactive incidents. Consider adding the term “reactive incident” to the four existing “release events”
in EPA’s current 5-year accident reporting requirements (Gas Release, Liquid Spill/Evaporation, Fire, and Explosion). Structure this information collection to allow EPA and its stakeholders to identify and focus resources on industry sectors that experienced the incidents; chemicals and processes involved; and impact on the public, the workforce, and the environment.

**National Institute of Standards and Technology (NIST)**

Develop and implement a publicly available database for reactive hazard test information. Structure the system to encourage submission of data by individual companies and academic and government institutions that perform chemical testing.

**Center for Chemical Process Safety (CCPS)**

1. Publish comprehensive guidance on model reactive hazard management systems. At a minimum, ensure that these guidelines cover:

   - For companies engaged in chemical manufacturing: reactive hazard management, including hazard identification, hazard evaluation, management of change, inherently safer design, and adequate procedures and training.

   - For companies engaged primarily in the bulk storage, handling, and use of chemicals: identification and prevention of reactive hazards, including the inadvertent mixing of incompatible substances.

2. Communicate the findings and recommendations of this report to your membership.
American Chemistry Council (ACC)

1. Expand the Responsible Care Process Safety Code to emphasize the need for managing reactive hazards. Ensure that:

   - Member companies are required to have programs to manage reactive hazards that address, at a minimum, hazard identification, hazard evaluation, management of change, inherently safer design, and adequate procedures and training.

   - There is a program to communicate to your membership the availability of existing tools, guidance, and initiatives to aid in identifying and evaluating reactive hazards.

2. Develop and implement a program for reporting reactive incidents that includes the sharing of relevant safety knowledge and lessons learned with your membership, the public, and government to improve safety system performance and prevent future incidents.

3. Work with NIST in developing and implementing a publicly available database for reactive hazard test information. Promote submissions of data by your membership.

4. Communicate the findings and recommendations of this report to your membership.

Synthetic Organic Chemical Manufacturers Association (SOCMA)

1. Expand the Responsible Care Process Safety Code to emphasize the need for managing reactive hazards. Ensure that:

   - Member companies are required to have programs to manage reactive hazards that address, at a minimum, hazard identification, hazard evaluation, management of change, inherently safer design, and adequate procedures and training.
- There is a program to communicate to your membership the availability of existing tools, guidance, and initiatives to aid in identifying and evaluating reactive hazards.

2. Develop and implement a program for reporting reactive incidents that includes the sharing of relevant safety knowledge and lessons learned with your membership, the public, and government to improve safety system performance and prevent future incidents.

3. Work with NIST in developing and implementing a publicly available database for reactive hazard test information. Promote submissions of data by your membership.

4. Communicate the findings and recommendations of this report to your membership.

National Association of Chemical Distributors (NACD)

1. Expand the existing Responsible Distribution Process to include reactive hazard management as an area of emphasis. At a minimum, ensure that the revisions address storage and handling, including the hazards of inadvertent mixing of incompatible chemicals.

2. Communicate the findings and recommendations of this report to your membership.

International Association of Firefighters

Paper, Allied-Industrial, Chemical & Energy Workers International Union (PACE)

The United Steelworkers of America

Union of Needletrades, Industrial, and Textile Employees (UNITE)

United Food and Commercial Workers International Union

American Society of Safety Engineers (ASSE)

American Industrial Hygiene Association (AIHA)

Communicate the findings and recommendations of this report to your membership.